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Review article

Nitride layers on uranium surfaces

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ABSTRACT

Uranium as an important energy material plays a significant role within the field of material sciences and nuclear industrial applications. However, metallic uranium is chemically active in ambient environment and is easily oxidized and corroded, leading to not only deterioration of its properties and failure of performance as working components but also nuclear pollution of the environment. Therefore, the development of corrosion protection systems for metallic uranium is an issue of prime importance. In view of the nitridation technology in Ti and Fe-based alloys, the successful application to improve the surface wear hardness and corrosion resistance, several nitridation methods have been developed for the surface modification of metallic uranium. Many studies have shown that the surface nitridation of metallic uranium can efficiently improve its corrosion resistance. The surface oxidation layer thickness is as thin as several nanometers even if placed 4 years in the atmosphere. At the present, nitridation of uranium surface is considered as the most promising surface modification way to protect uranium from corrosion. To design and fabricate nitride layers on uranium surface with reliable long-term protective effects, however, one needs deep understanding on the relationships among the physical and chemical properties of the nitride layers, the composition and structure of the layers, and the dependence on the techniques and the processing parameters. One also needs deep understanding on the corrosion behavior of the prepared nitride layers in the environment, and the related corrosion mechanism.

In this review, we bring to the readers the achievements and recent advances on the uranium nitridation in the world, including the processing techniques and the related studies on the formation mechanism of the nitride layers, and the understanding on the property-processing-corrosion performance relationship of the layers, aiming at the development of high-performance resistance layers for metallic uranium by the surface nitridation technique. In the review (1) the surface nitridation techniques developed recently, the relationship between the preparation parameters and the composition as well as the structure of the surface layer are summarized; (2) the fundamental physical properties of the uranium nitrides are summarized, depicted and discussed; (3) the influence of the nitrides structure and composition and of the environment on resistance to corrosion as well as the formation mechanism of corroded products in oxidizing environments are depicted and discussed; (4) the potential application of uranium nitrides in other application field such as the application of thermal-electrical conversion is also discussed. Finally, the prospective on the investigations of nitride layers is suggested.

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1. Introduction

Uranium, as an important energy material, plays a significant role in the fields of material sciences and nuclear industrial applications [1]. However, metallic uranium is chemically active in ambient environment and is easily oxidized and corroded, leading to not only deterioration of its properties and failure of performance as working components but also nuclear pollution of the environment. The corrosion behavior of metallic uranium in various atmospheres has been studied systematically and reviewed [1,2]. Some important items related to uranium corrosion are summarized in brief. From these studies it is known that the prime products of depleted uranium in dry oxygen atmosphere are uranium oxides, yet the uranium valence state was found dependent on the oxygen partial pressure, the reaction temperature, e.g., [3]. In addition, the corrosion kinetics of uranium is dramatically affected by the presence of water vapor [4,5]. Therefore, it is of great significance to devise methodologies for protecting metallic uranium from corrosion based on the knowledge obtained from the corrosion behavior of uranium.

In the past decades, progress has been made in developing techniques to protect metallic uranium from corrosion. These techniques fall briefly into two categories: (1) Bulk treatment technique. For example, the alloying method is an important way [6,7]. It has been found effective in protecting uranium from corrosion by alloying with a small amount of other metals like Titanium, Niobium, Zirconium and Ruthenium, etc., which also substantially altered its mechanical properties [7]. The inevitable involvement of additional metallurgical defects, e.g., inhomogeneous distribution of the alloying elements concentration, the introduction of heterogeneous impurities, however, is a drawback of this technique. In addition, a slight excess of the amount of the alloying elements may affect largely the nuclear properties of the metallic uranium, thus limiting the applications of the uranium alloys. (2) Surface treatment technology based on surface science, for example, isolating the surface of metallic uranium from the environment media by coating or plating its surface with inert layers [8], or modifying its surface to form a passivation layer by a variety of techniques such as chemical reaction, ion beam bombardment, etc., [9–15]. Surface treatment technology has been widely used in improving the corrosion resistance of metallic uranium, and has been proven effective [11–16]. For instance, chemical vapor deposition (CVD) and physical vapor deposition (PVD) approaches have been frequently employed to produce coating layers on metallic uranium as corrosion barriers in corrosive media from 1960s to 80s. The coatings produced by these approaches can improve the corrosion resistance of uranium to some extent, yet with a poor adhesive strength on uranium surface. Since 1980s, ion implantation and surface diffusion treatment technologies such as surface nitridation, surface carburization and surface alloying, etc., have been utilized to modify the chemical composition, morphology and microstructure of uranium surface to improve its corrosion resistance. The results have played a momentous role in improving the corrosion resistance of uranium materials [17,18]. Especially, the research on the surface nitridation of uranium materials is the most comprehensive and systematic, so as to realize the long-term and effective corrosion resistance of uranium materials. Among these approaches, it has been found that the surface nitridation could be a promising technique to realize the long-term effective protection of metallic uranium from corrosion. This is because substantial studies have shown that uranium nitrides, such as UN and U_2N_3, have good corrosive resistance to the atmosphere, water (steam), oxygen etc., and that adhesion of the modified surface layer on uranium was largely improved as this layer is gradient in both composition and microstructure [11–16,19,20].

To date, several nitridation methods have been developed for the surface modification of metallic uranium. Arkush et al. modified the surface of uranium by nitrogen ion implantation. They observed the formation of a gradient uranium nitride layer on the surface, which improved the adhesion strength between the film and the metallic uranium. The nitride layer exhibited greatly improved oxidation resistance, *i.e.*, the surface oxidation layer was only several nanometers thick after 4 years in atmosphere [12]. In the past decade, our group has employed ion beam implantation, laser and glow plasma nitridation technologies to form various uranium nitrides on the uranium surface, and studied systematically the electronic structure, thermal and electrical properties, and the corrosion behavior of the uranium nitrides [13–16,19–30]. The nitride layers prepared by these methods also display excellent corrosion resistance at room temperature in the atmosphere.

At the present, nitridation of uranium surface is considered as the most promising surface modification way to protect uranium from corrosion. To design and fabricate nitride layers on uranium surface with reliable long-term protective effects, however, one needs deep understanding on the relationships among the physical and chemical properties of the nitride layers, the composition and structure of the layers, and the dependence on the techniques and the processing parameters. One also needs deep understanding on the corrosion behavior of the prepared nitride layers in the environment, and the related corrosion mechanism.

In this review, we bring to the readers the achievements and recent advances on the uranium nitridation in the world, including the processing techniques and the related studies on the formation mechanism of the nitride layers, and the understanding on the property-processing-corrosion performance relationship of the layers, aiming at the development of high-performance resistance layers for the metallic uranium by the surface nitridation technique. Firstly, the surface nitridation techniques developed recently, the relationship between the preparation parameters and the composition as well as the structure of the surface layer are summarized. Secondly, the fundamental physical properties of the uranium nitrides are summarized, depicted and discussed. Thirdly, the influence of the nitrides structure and composition and of the environment on resistance to corrosion as well as the formation mechanism of corroded products in oxidizing environments are depicted and discussed. Fourthly, the potential application of uranium nitrides in other application field such as the application of thermal-electrical conversion is also discussed. Finally, the prospective on the investigations of nitride layers is suggested.